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AN EXACT QUANTUM STUDY OF VIBRATIONAL DEACTIVATION BY REACTIVE --ETC(U)  
AUG 76 G C SCHATZ, A KUPPERMANN AFOSR-73-2539  
CONTRIB-5284

AFOSR-TR-78-0833

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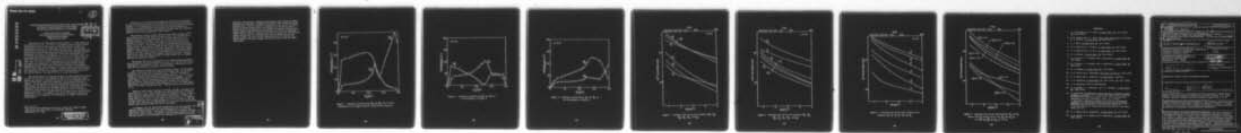


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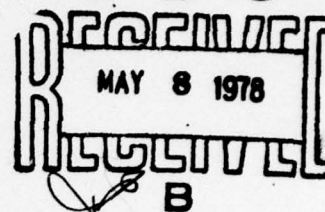
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AN EXACT QUANTUM STUDY OF VIBRATIONAL DEACTIVATION  
BY REACTIVE AND NONREACTIVE COLLISIONS  
IN THE COLLINEAR ISOTOPIC H + FH SYSTEMS\*

D D C

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The success of the HF chemical laser depends to a large extent on the relative rates of: (1) the F + H<sub>2</sub> pumping reaction which produces vibrationally excited HF(v), and (2) the deactivation of HF(v) by collisions with H<sub>2</sub>, F, H, buffer gas, and HF itself. Although the deactivation of HF by H<sub>2</sub>,<sup>1</sup> F,<sup>2</sup> and HF<sup>3</sup> has been both experimentally and theoretically well-characterized with generally good agreement between experiment and theory, the situation is far less satisfactory for H + FH and its isotopic counterparts, D + FD, H + FD, and D + FH. The three experimental determinations of the H + FH (v = 1) deactivation rate<sup>2,4,5</sup> give rate constants at 300°K of  $< (7 \pm 4) \times 10^{11}, 4 \leq 9 \times 10^9,$ <sup>2</sup> and  $(1.4 \pm 0.4) \times 10^{11}$  cm<sup>3</sup>/mole-sec,<sup>5</sup> thus disagreeing with one another by amounts well outside their respective error limits. Agreement with the results of a theoretical (classical trajectory) calculation of this rate constant is no better with a predicted value of  $2.2 \times 10^{12}$  cm<sup>3</sup>/mole-sec at 300°K. Similar experimental and theoretical comparisons of the rate constants for the deactivation of D + FD (v = 1), D + FH (v = 1), and H + FD (v = 1) are also poor.<sup>5</sup>

The approximation of classical dynamics has been analyzed in detail for the F + H<sub>2</sub><sup>7</sup> and F + D<sub>2</sub><sup>8</sup> reactions, and its most important consequences for reactive collisions were found to be an inadequate description of resonances, neglect of tunneling, and dynamical threshold effects. In considering vibrational deactivation processes, we must also examine the validity of the quasi-classical prediction<sup>6</sup> that multi-quantum jump transitions are extremely important in deactivating collisions (both nonreactive and reactive) for H + FH. If true, it could be important, for it would mean that H atoms can be very efficient deactivators of HF. In addition, much of the theoretical analysis is predicated on the assumption of the dominance of single quantum jump transitions.<sup>9</sup>

\*This research was supported in part by a grant (No. AFOSR-73-2539) from the US Air Force Office of Scientific Research.

†Contribution No. 5284.

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In this paper we examine the dynamics of reactive and nonreactive  $H + FH$  and its isotopic counterparts using accurate quantum mechanical methods. In all calculations we restrict our considerations to collinear collisions, an approximation which renders the quantum mechanical problem tractable while still retaining many of the important dynamical features of the three-dimensional (3-D) world.<sup>10,11</sup>

The potential energy surface used was Muckerman's Surface Five<sup>12,13</sup> whose LEPS parameters are given by Schatz et al.<sup>7</sup> This surface has a barrier height of 1.23 kcal/mole for the collinear  $H + FH \rightarrow HF + H$  exchange reaction. Recently, Bender et al.<sup>14</sup> have shown that this barrier is seriously in error, the correct value being estimated at about 40 kcal/mole. The present results may nevertheless be qualitatively correct if the quantum number of the initial vibrational states considered are increased so as to place these states above the correct barrier. Those features of the results depending on the atomic masses (such as the skew angle between the coordinate axis in terms of which the kinetic energy operator is diagonal) should be correct. Calculations of the effect of barrier height on these results are in progress and will be presented elsewhere.

The method used in the calculation was a coupled-channel propagation technique<sup>15</sup> previously applied to  $H + H_2$ ,<sup>16</sup>  $F + H_2$ ,<sup>7,17</sup> and  $F + D_2$ .<sup>8</sup> Convergence, conservation of flux, and microscopic reversibility indicate that the results are accurate to 1% or better.

The transition probability from vibrational state  $v$  of the reagent to state  $v'$  of the product is denoted by the symbol  $P_{vv'}^R$ , for reactive collisions and by  $P_{vv'}^V$ , for nonreactive ones. Figures 1 through 3 display the reactive and nonreactive probabilities  $P_{3v'}$  ( $v' = 0, 1, 2$ ) as a function of the relative kinetic energy  $E_3$  of the reagents. In all these figures, reactive probabilities exceed the nonreactive ones in the low kinetic energy region important for thermal rate constants. Furthermore, the multiquantum jump probabilities are of the same magnitude as the single quantum jump ones. Similar results are obtained for  $v = 2$ .

Figures 4 and 5 depict several of the  $k_{vv'}^R$  and  $k_{vv'}^V$ , collinear rate constants for  $H + FH$ . They indicate that the reactive rate constants are in general significantly larger than the nonreactive ones. Figure 6 shows the total deactivation rate constants  $k_v^R$  and  $k_v^V$ . At 300°K, the ratio  $k_v^R/k_v^V$  is 8.3 for  $v = 1$ , 8.5 for  $v = 2$ , and 3.5 for  $v = 3$ . Figure 7 contains Arrhenius plots of  $k_{10}^R$  and  $k_{10}^V$  for  $H + FH$ ,  $D + FD$ ,  $H + FD$ , and  $D + FH$ , which indicate that substitution of H by D does not qualitatively affect these results, except for the  $H + FD$  system.

In summary, for all transition probabilities and rate constants the reactive mechanism dominates over the nonreactive one in producing vibrational deactivation. This result is apparently of general validity over a wide range of impact parameters since the same conclusions (even the same ratios of rate constants) were obtained by Wilkins<sup>6</sup> in his 3-D

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classical calculations. Secondly, multiquantum jump transition probabilities are comparable in magnitude to single quantum jump transition probabilities. This is clearly a consequence of the use of a reactive potential energy surface since the analogous  $H + HF$  results (for a surface which is nonreactive at the energies considered) indicate that single quantum jump transition probabilities are orders of magnitude larger than all others. Finally, we should reiterate that the potential energy surface used is of questionable validity because of its low barrier height, but that similar results may still be obtained for higher barriers for those reagent vibrational states which lie above the barrier.

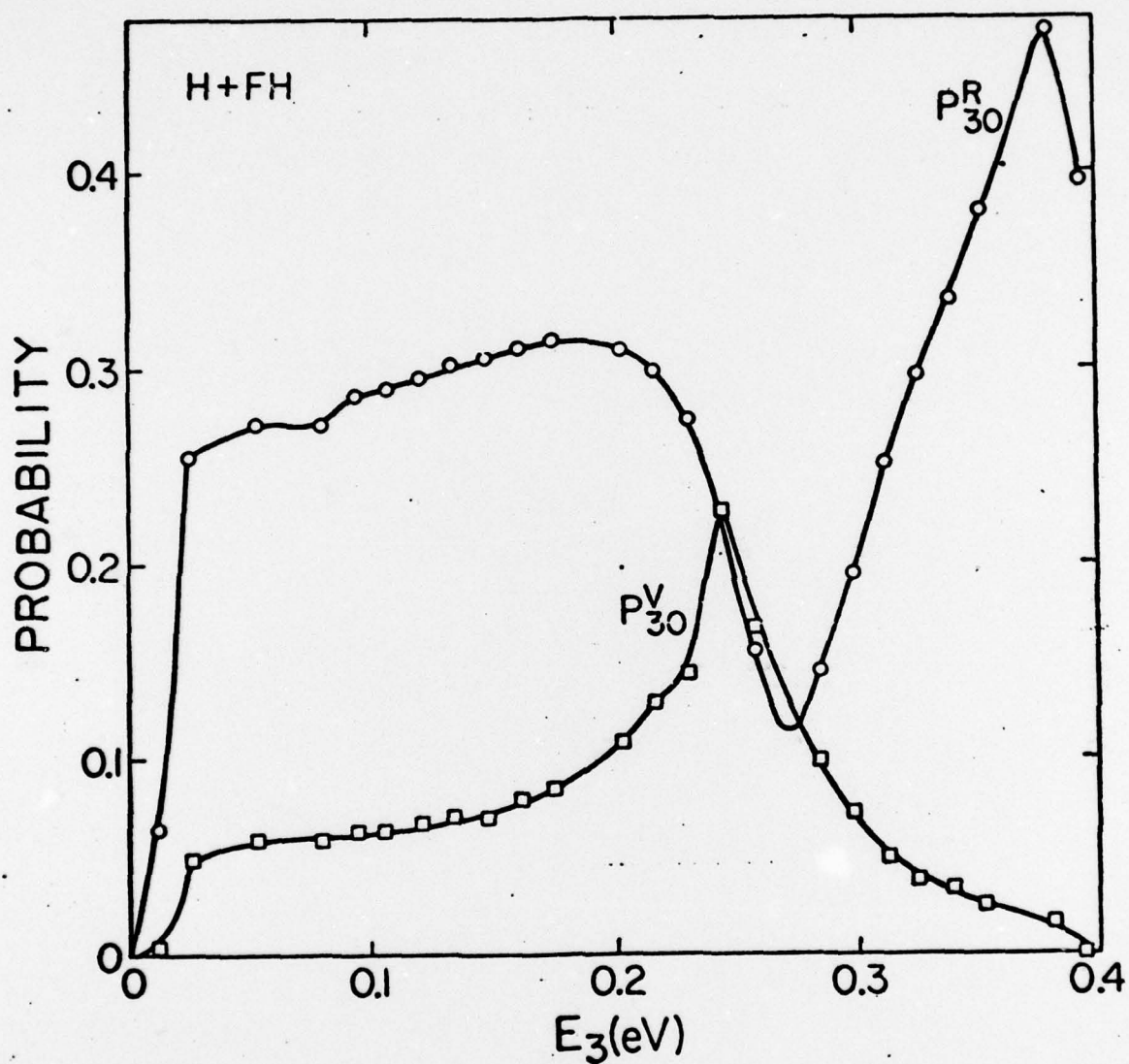


Figure 1. Transition probabilities  $P_{30}^R$  and  $P_{30}^V$  for  $H + FH$  as a function of the reagent relative translational energy  $E_3$ .

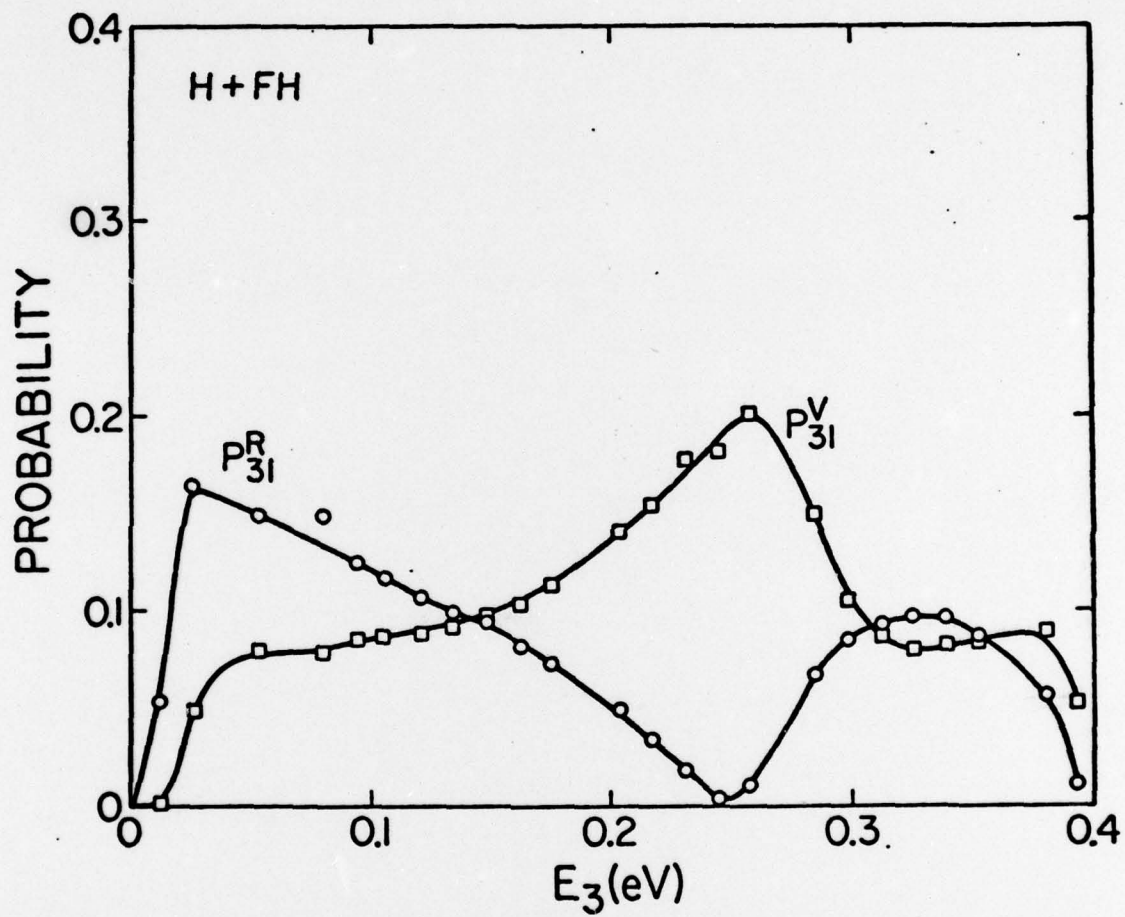


Figure 2. Transition probabilities  $P_{31}^R$  and  $P_{31}^V$  for  $H + FH$  analogous to Figure 1.



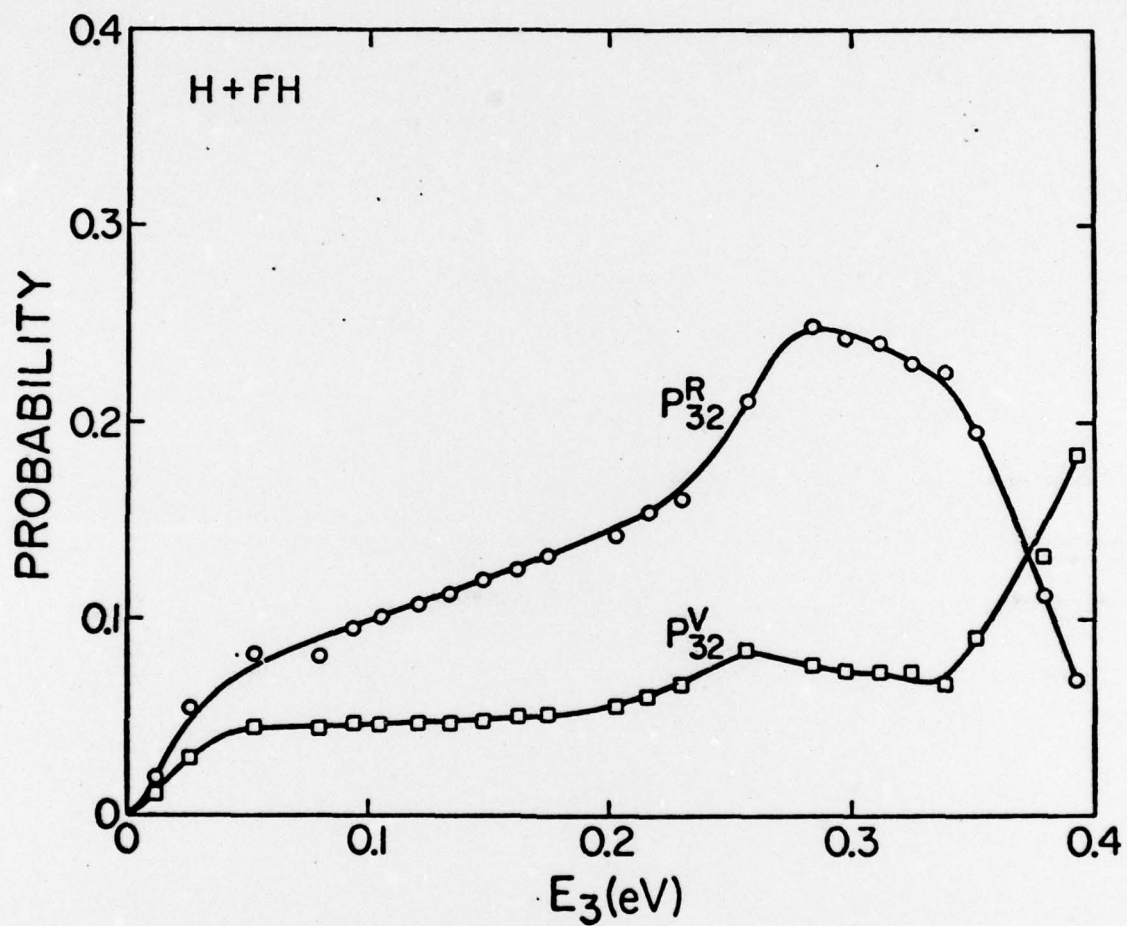


Figure 3. Transition probabilities  $P_{32}^R$  and  $P_{32}^V$  for  $H + FH$  analogous to Figure 1.

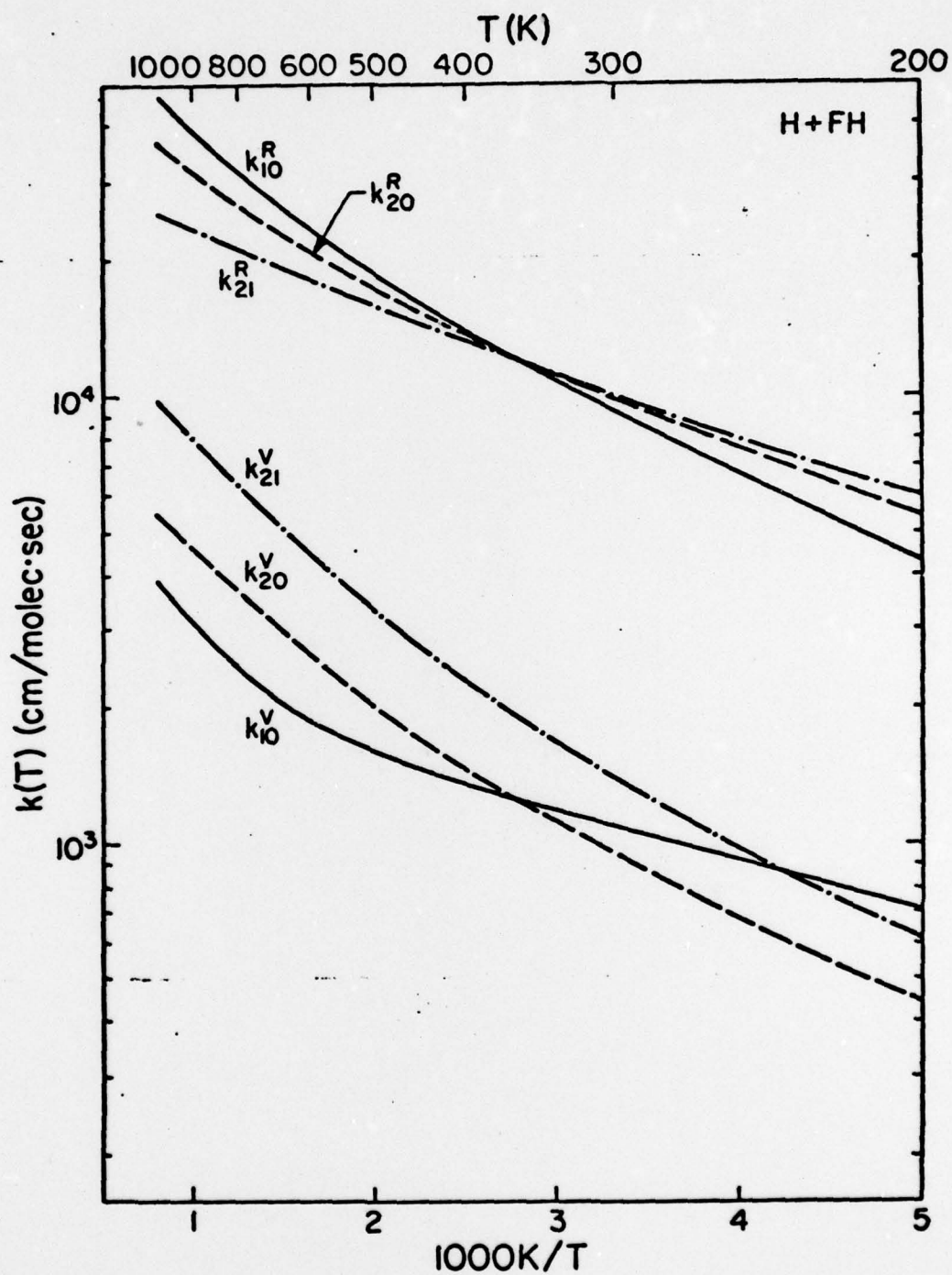


Figure 4. Arrhenius plot of the rate constants  $k_{10}^R$ ,  $k_{10}^V$ ,  $k_{20}^R$ ,  $k_{20}^V$ ,  $k_{21}^R$ , and  $k_{21}^V$ .



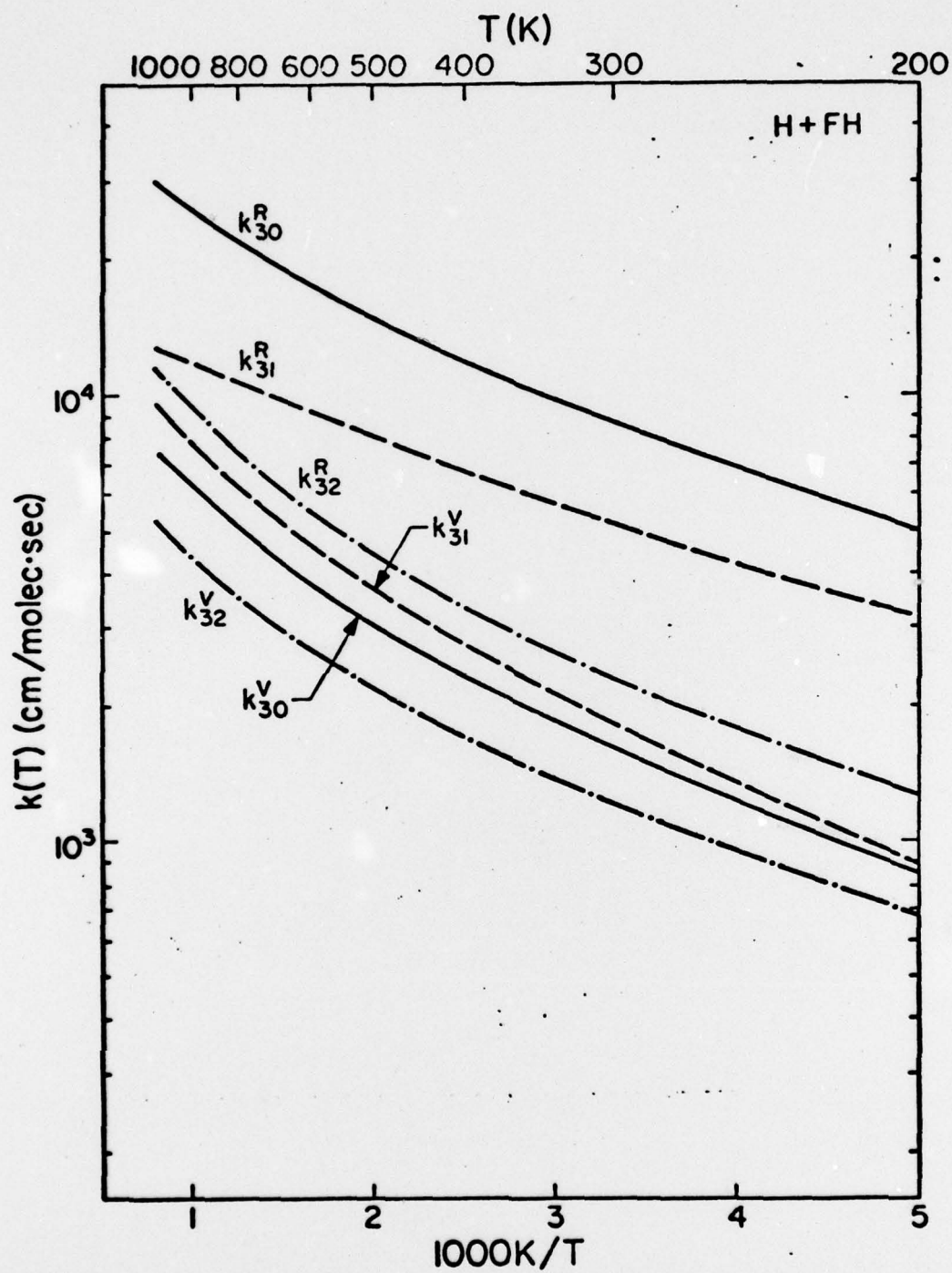


Figure 5. Arrhenius plot of the rate constants  $k_{30}^R$ ,  $k_{30}^V$ ,  $k_{31}^R$ ,  $k_{31}^V$ ,  $k_{32}^R$ , and  $k_{32}^V$ .

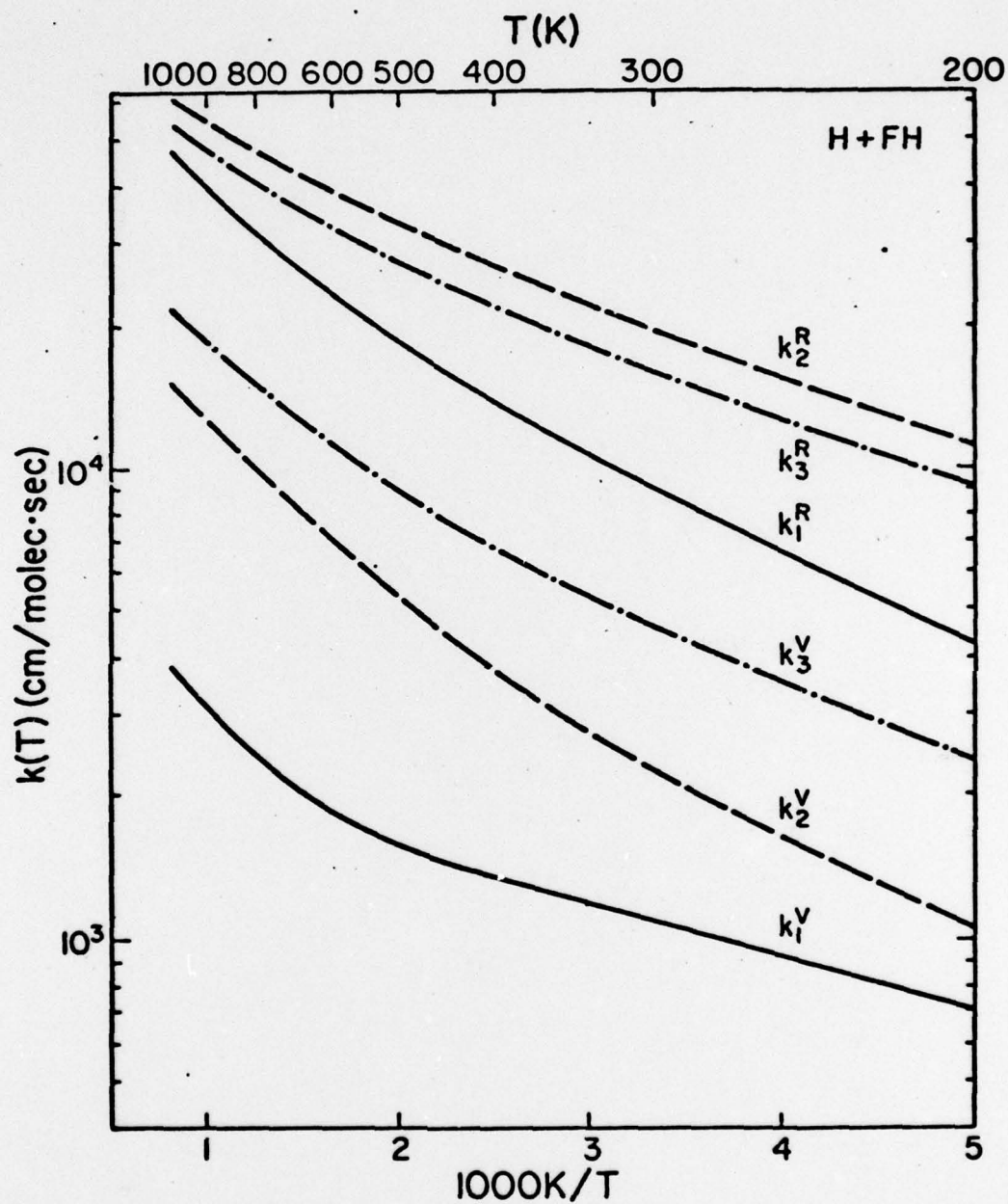


Figure 6. Arrhenius plot of the total inelastic rate constants  $k_1^R$ ,  $k_1^V$ ,  $k_2^R$ ,  $k_2^V$ ,  $k_3^R$ , and  $k_3^V$ .

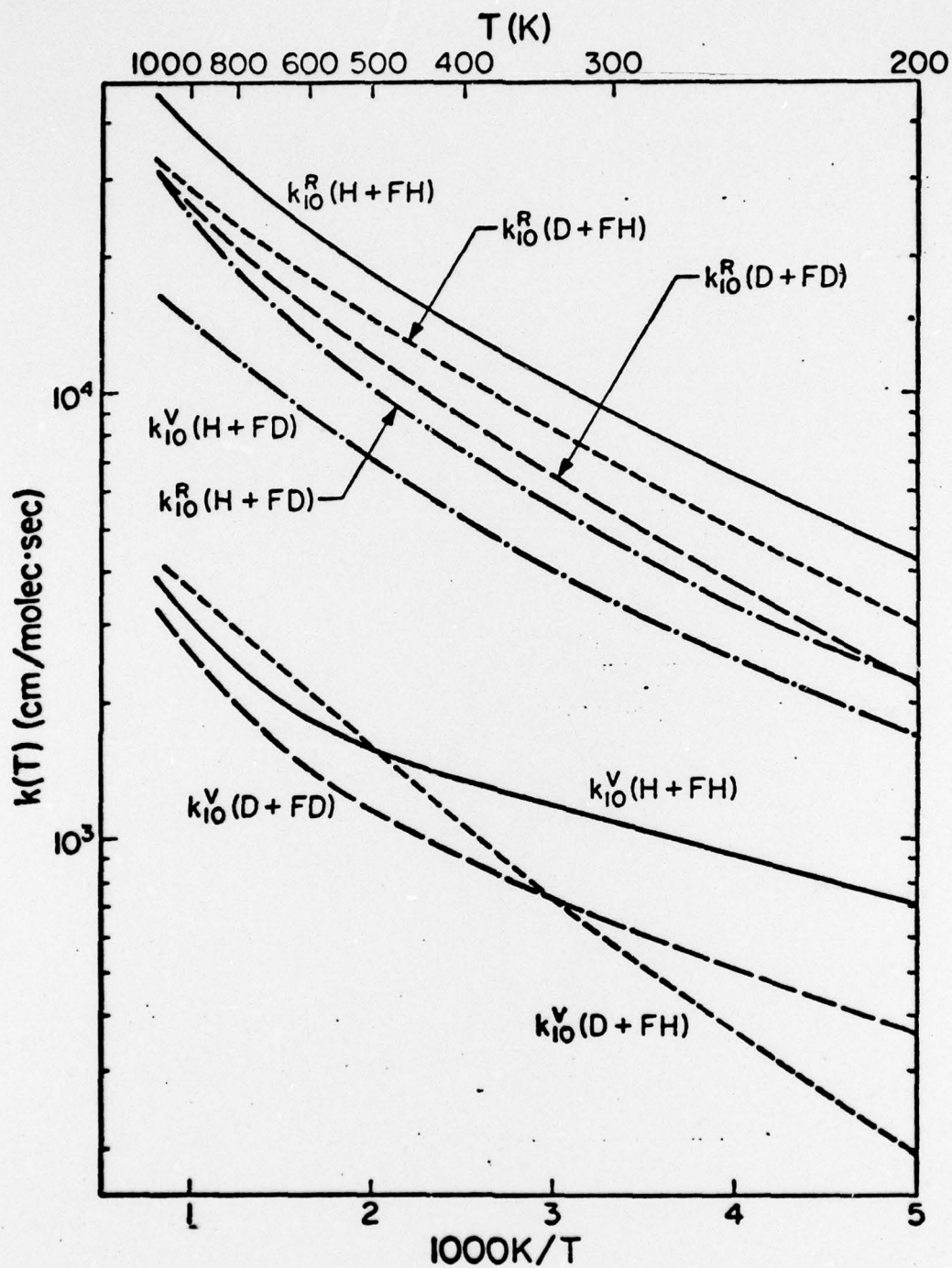


Figure 7. Arrhenius plot of the rate constants  $k_{10}^R$  and  $k_{10}^V$  for  $H + FH$ ,  $k_{10}^R$  and  $k_{10}^V$  for  $D + FD$ ,  $k_{10}^R$  and  $k_{10}^V$  for  $D + FH$ , and  $k_{10}^R$  and  $k_{10}^V$  for  $H + FD$ .



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1. REPORT NUMBER AFOSR/TR- 78 - 0833	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle) AN EXACT QUANTUM STUDY OF VIBRATIONAL DEACTIVATION BY REACTIVE AND NONREACTIVE COLLISIONS IN THE COLLINER ISOTOPIC H + FH SYSTEMS.		5. TYPE OF REPORT & PERIOD COVERED Interim report	
7. AUTHOR(s) George C. Schatz and Aron Kuppermann		8. CONTRACT OR GRANT NUMBER(s) AFOSR-73-2539	
9. PERFORMING ORGANIZATION NAME AND ADDRESS Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B1	
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research/NC Bolling AFB, Building 410 Washington, D.C. 20332		12. REPORT DATE Aug 1976	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (14) Contrib 5284		13. NUMBER OF PAGES (12) 12 p.	
		15. SECURITY CLASS. (of this report) UNCLASSIFIED	
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE	
16. DISTRIBUTION STATEMENT (of this Report)  Approved for public release; distribution unlimited.			
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  PE 61102F (16) 2303 (17) B1 W4 AFOSR 2303 B1			
18. SUPPLEMENTARY NOTES Special Report RH-7T-1, Proceedings of Army Symposium on High Energy Lasers: Current Problems in High Energy Transfer Lasers, U. S. Army Missile Command, Redstone Arsenal, Alabama, August 1976. p132-142			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) quantum mechanical transition probabilities; rate constants; vibrational deact- ivation; reactive and nonreactive collisions; collinear H + FH(V), D + FH(v), H + FD(v), and D + FH(v); rate constants; nonreactive and reactive transition probabilities; multiquantum jump transitions; deactivators.			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Accurate quantum mechanical transition probabilities and rate constants for vibrational deactivation via reactive and nonreactive collisions in collinear H + FH(v), D + FD(v), H + FD(v), and D + FH(v) are presented. In all cases, the reactive inelastic rate constants are larger than the nonreactive ones for the same initial and final vibrational states, but the ratios of these reactive and nonreactive rate constants depend strongly on the vibrational quantum number v and on isotopic composition of the reagents. Nonreactive and react- ive transition probabilities for multiquantum jump transitions are generally →			

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comparable to those for single quantum transitions. This vibrationally non-adiabatic behavior is a direct consequence of the severe distortion of the diatomic that occurs in a collision on a reactive potential surface, and makes H or D more efficient deactivators of HF or DF than are nonreactive collision partners. Most conclusions are in qualitative and even quantitative agreement with those of Wilkins' three-dimensional quasi-classical trajectory study on the same systems.



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